AD-A052 407 IMPERIAL COLL OF SCIENCE AND TECHNOLOGY LONDON (ENGLAND) F/G 11/6
THE ROLE OF HYDROGEN IN THE STRESS CORROSION FAILURE OF HIGH ST--ETC(U)
JAN 78 L CHRISTODOULA, G LACKEY, H M FLOWER DA-ERO-77-G-011

UNCLASSIFIED NL

| OF |
AD
A052407

END
DATE
FILMED
5 -78
DDC

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER

2. GOVT ACCESSION NO.

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle)

The Role of Hydrogen in the Stress Corrosion Failure of High Strength Al-Zn-Mg Alloys and Sensitised Austenitic Stainless Steels.

5. TYPE OF REPORT & PERIOD COVERED

Annual Technical Report. Jan[redacted] 77 — Jan[redacted] 78,

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s)

L. Christodoula, G. Lackey, H.M. Flower, F.J. Humphreys, P.R. Swann

8. CONTRACT OR GRANT NUMBER(s)

DA-ERO-77-G-011

DAERO-77-G-011 new

9. PERFORMING ORGANIZATION NAME AND ADDRESS

Imperial College
London, U.K.

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS

6.11.02A 1T 161102BH57-011-00-615

11. CONTROLLING OFFICE NAME AND ADDRESS

US Army R&S Gp (Eur)
Box 65, FPO NY 09510

12. REPORT DATE

Jan[redacted] 1978

13. NUMBER OF PAGES

27 27P.

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)

15. SECURITY CLASS. (of this report)

UNCLASSIFIED

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for Public Release - Distribution Unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Hydrogen Embrittlement, Stress Corosion, Sensitised Stainless Steel, Al-Mn-Zn Alloys.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

SEE BACK

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

176 350

JOB

This first annual report covers work carried out over a full year on the environment sensitive failure of high strength Al-Zn-Mg alloys and the first three months work on the failure of austenitic stainless steels. The report is divided into two parts covering each of the materials studied.

Part 1.

It has been found that exposure of an Al-Zn-Mg alloy to water vapour saturagated air results in loss of ductility and subsequent formation of hydrogen bubbles at high energy sites such as grain boundaries. The rate of embrittlement depends upon the prior heat treatment of the alloy: thus for a given hydrogen level one microstructure may be brittle while another may still exhibit some ductility.

Fractographic studies have indicated that the distribution of hydrogen within the alloy determines the mode of fracture.

Part 2.

Experimental techniques have been developed to study the stress corrosion of stainless steel. Preliminary characterisation of the material (302 grade stainless steel) is in progress.

In both parts of the report proposed future studies are described.

AD

The Role of Hydrogen in the Stress Corrosion Failure of High Strength Al-Zn-Mg Alloys and Sensitised Austenitic Stainless Steels.

Annual Technical Report

By

L. Christodoulou, G. Lackey, H.M. Flower, F.J. Humphreys and P.R. Swann

January, 1978

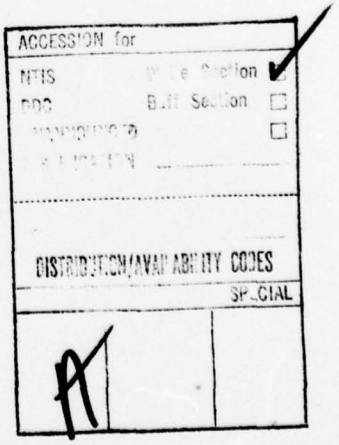
EUROPEAN RESEARCH OFFICE

United States Army

London England

GRANT NUMBER DA-ERO-77-G-011

Imperial College



SUMMARY

This first annual report covers work carried out over a full year on the environment sensitive failure of high strength Al-Zn-Mg alloys and the first three months work on the failure of austenitic stainless steels. The report is divided into two parts covering each of the materials studied.

Part 1.

It has been found that exposure of an Al-Zn-Mg alloy to water vapour saturated air results in loss of ductility and subsequent formation of hydrogen bubbles at high energy sites such as grain boundaries. The rate of embrittlement depends upon the prior heat treatment of the alloy: thus for a given hydrogen level one microstructure may be brittle while another may still exhibit some ductility.

Fractographic studies have indicated that the distribution of hydrogen within the alloy determines the mode of fracture.

Part 2.

Experimental techniques have been developed to study the stress corrosion of stainless steel. Preliminary characterisation of the material (302 grade stainless steel) is in progress.

In both parts of the report proposed future studies are described.

CONTENTS

Part 1. Aluminium-Zinc Magnesium Alloys	Page
1. Introduction	2
2. Literature survey	2
3. Experimental procedure	2
4. Results	4
4.1. Mechanical tests and fractography	4
4.2. Effect of prestraining	5
4.3. High voltage electron microscopy	5
5. Discussion of experimental results	7
6. Experimental techniques under development and proposed future work	9
6.1. Hydrogen analysis	9
6.2. Monocrystals	10
6.3. In-situ experiments	10
6.4. Cathodic charging	11
6.5. Tracer analysis	11
7. Conclusions	12
Part 2. Austenitic Stainless Steel	
(a) Abstract	12
(b) Research to date	12
1. Material	12
2. Heat treatment	12
3. Electron microscopy	13
4. Mechanical testing	13
(c) Proposed research	13
1. Pre-exposure tests	13
2. Environmental tests	13
3. Electron microscopy	13
References	14
Table 1	15
Graphs	16
Figures	18

Part 1. Aluminium-Zinc-Magnesium Alloys

1. Introduction

The role of hydrogen in the environment sensitive failure of a high strength aluminium alloy has been studied by employing the pre-exposure embrittlement phenomenon. In previous studies [1,2] this phenomenon was shown to be closely related to stress corrosion cracking and the results strongly suggested that hydrogen embrittlement was the predominant mechanism of intergranular failure.

In this report the results of further experiments on the pre-exposure embrittlement effect will be presented, but before giving these the results of previous work in the field will be briefly reviewed.

2. Literature Survey

The pre-exposure embrittlement effect was first reported by Gruhl [3] who found that specimens of a high purity Al-Zn-Mg alloy suffered reductions in stress corrosion life and ductility if they had previously been exposed to a 2%NaCl solution. A similar effect was found in the case of pre-exposure to moist gases and this has been reported in detail elsewhere [1,2,4]. In that work embrittlement was associated with the presence of hydrogen in the grain boundaries as evidenced by the evolution of hydrogen upon fracture and the presence of hydrogen bubbles along the grain boundaries.

Experiments by Gest and Troiano [5] revealed that cathodic charging reduced the ductility of a commercial 7075 alloy. Their results have been recently confirmed by Bernstein and Thompson et al [6]. These workers have found that following cathodic charging the 7075 alloy (table I) exhibits the characteristics of classical hydrogen embrittlement. In agreement with such a mechanism strain rate sensitivity and test temperature dependence of ductility were observed. Permeability measurements indicated a close relationship between stress corrosion crack velocity and hydrogen permeability.

3. Experimental Procedure

The alloy used in this investigation was a high purity Al-Zn-Mg alloy supplied by Alcan U.K. The composition is listed in Table I. 250 mm thick slabs were sliced from the supplied cast billet, initially hot rolled, and finally cold rolled down to a thickness of 0.5 mm. The oxide formed during the working sequence was removed by chemical

polishing in a concentrated NaOH solution. No further surface preparation was carried out.

The standard heat treatment, following the working sequence, consisted of a solution treatment of 450°C for 1 hour followed by a cold water quench. This resulted in a completely equiaxed structure of grain size of 20-25μm.

All heat treatments, including subsequent ageing, were carried out under a dry, high purity argon atmosphere to minimise the effect of any water vapour present in the furnace atmosphere.

Pre-exposure experiments were carried out in sealed vessels where the specimens were placed above a pool of distilled water. Dry, control specimens, were placed in sealed, argon containing glass tubes to exclude water vapour and placed at positions adjacent to the exposed ones.

High temperature exposure tests were carried out in an autoclave at a temperature of 120°C and 2.06 bars (.206 MN/m^2) pressure. Specimens were solution treated at 450°C for 1 hour, cold water quenched and then placed in the autoclave. Thus, both ageing and pre-exposure were occurring simultaneously. Again dry control samples sealed in glass capsules were also employed.

Metallographic examination of specimens was conducted in transmission using the A.E.I. EM7 high voltage microscope and in reflection using a Cambridge 600 and a JEOL TEMSCAN 100C scanning electron microscopes.

High voltage microscopy is essential in this work since the presence of hydrogen and its interactions with grain boundaries is of vital importance. Thick foils are needed a) to prevent excessive loss of hydrogen to the surfaces and b) so that large boundary areas can be studied under a large variety of orientations in order to establish unequivocally the presence of hydrogen bubbles.

The facilities of the environmental cell, heating and bending stages are also available on this microscope.

Specimen preparation for transmission electron microscopy (TEM) was carried out using a standard surface preparation technique in a 20% perchloric acid - ethanol solution at -20°C and at a potential of 20 volts. Additionally a small number of samples were electropolished in 30% nitric acid in methanol at -10°C and at a potential of 12 volts: also selected samples were ion beam thinned using argon at 5.6 KV after

polishing down to 60-80um. These latter techniques were used to determine whether the surface preparation technique affected the results by introducing artifacts into the samples.

4. Results

4.1. Mechanical Tests and Fractography

In order to determine the effect of ageing time on the pre-exposure effect a series of mechanical tests was carried out on pre-exposed specimens. The samples were given the standard heat treatment followed by ageing at the desired temperature (70-250°C) for 24 hours (under argon). They were then given a pre-exposure treatment consisting of 72 hours in water vapour saturated air (w.v.s.a.) at 70°C. The results are shown in Graph I. It can be seen that the maximum loss of ductility occurs after ageing at 120°C for 24 hours which is in excellent agreement with results from stress corrosion tests [7].

Further pre-exposure experiments were carried out in an autoclave at 120°C. The results are shown in graph II. A number of points are to be noted from this graph.

Firstly both dry and wet specimens show a reduction in ductility at the same rate for times up to 5 hours. This is due to the precipitation reaction which occurs in all specimens. A correspondingly high rate of increase of yield stress is associated with this region.

At longer exposure times the rate of ductility loss of the pre-exposed specimens continues to be high and total embrittlement is apparent after 10 hours while dry samples remain ductile at the 2% level and finally show an increase after 38 hours reflecting the onset of overageing (graph II.).

The most striking feature of the graph occurs after an exposure time of 24 hours when a sudden increase in ductility of exposed samples is apparent. (This behaviour is not found in dry specimens.) The increased ductility is maintained for about 8 hours and then rapidly disappears with the specimen failing at very low stresses and 0% ductility. Fracture in this latter region is exclusively at the grips of the specimens.

Fractography of the tested, pre-exposed specimens in the three regions II, III, IV, has produced the following results.

a) Region II.

A brittle intercrystalline failure was found with flat fracture facets (Fig. 1) In some cases transgranular cracks were initiated but

the intercrystalline mode of failure predominated (Fig. 2). Where large intermetallic particles were present, voids were found to be associated with them together with some evidence of ductile tearing (Fig.3).

b) Region III.

This region exhibited two distinct transitions in fracture morphology from an intercrystalline band at the exterior via a transgranular cleavage band, to a ductile central core (Fig. 4). Crack branching was also apparent in this state.

c) Region IV.

Region IV was found to have returned to an intercrystalline faceted mode of failure. This time, however, grain boundary precipitates were clearly observed on the fracture surfaces, some being surrounded by depressions. Significantly it was noted that not all grain boundaries were surrounded by these depressions. Figure 5 shows that two adjacent grain boundaries can differ considerably. In one grain boundary every precipitate was found to be surrounded by a void while this was only an occasional occurrence on the second grain boundary. No evidence of plastic tearing was found.

4.2. Effect of Prestraining

Since samples in region IV failed at the holes in the grip regions of the specimens it was thought possible that residual stresses in these regions might have increased the embrittlement during exposure in the autoclave. Therefore, several specimens were deformed in tension to a 10% plastic elongation and were then placed in the autoclave. These formed cracks within 5 hours of exposure and were too brittle for mechanical testing to be possible. These results suggest that cold working accelerates the embrittlement phenomenon. It remains to be determined whether this is due to residual stresses or whether it is also affected by the changes in dislocation density and distribution.

4.3. High Voltage Electron Microscopy

High voltage transmission electron microscopy (HVEM) has revealed the existence of hydrogen bubbles in region IV (Fig. 6), while no such evidence has been found in regions II and III. No bubbles were observed under any circumstances in any dry specimens.

Appearance of bubbles was limited to heavily pre-exposed specimens, *i.e.* total loss of ductility occurred long before bubbles were observed

in the electron microscope. This suggests that embrittlement is not directly caused by the existence of hydrogen bubbles, but rather by a high level of hydrogen in solution at the grain boundaries.

In overaged specimens large precipitates were present at the grain boundaries and the bubbles were found to have nucleated preferentially at these sites. In all specimens it was apparent that some grain boundaries were much more prone to bubble formation than others. It was therefore concluded that the nucleation of bubbles is a complex phenomenon not unlike precipitate nucleation. It is suggested that the nucleation will depend on the grain boundary/precipitate orientation relationship: incoherent interfaces offering the best sites. Also the grain boundary structure is expected to be important. It was noted that the grain boundaries with the greatest density of bubbles were of the random high angle type. Similar observations have been made previously concerning particle nucleation at grain boundaries [8].

Some evidence was found that bubbles also formed on dislocations attached to grain boundaries (Fig. 7). This may imply rapid passage of hydrogen from the boundary down dislocations: if so it might explain the rapid embrittlement of pre-strained samples during exposure in the autoclave. Hydrogen might proceed rapidly through material containing a high dislocation density and tend to segregate in regions of high hydrostatic tensile stress.

Growth of bubbles under the electron beam was also observed. This had the drawback of making the estimation of bubble size difficult but had a distinct advantage in dry specimens where any strain fields around grain boundary particles could be examined under the beam in the fully condensed condition. The strain fields could be studied under a range of imaging conditions and lack of growth after 15 minutes was taken as positive proof that the strain field was due only to the particle and not to hydrogen.

The two different electropolishing solutions used, perchloric-ethanol and nitric-methanol gave identical results. Ion beam thinning where the specimen never came into contact with any electropolishing solution, resulted in lower quality foils, due to radiation damage, but nevertheless revealed the existence of bubbles, thus positively proving that bubbles are not an electropolishing artifact but are due to the pre-exposure to the moist environment.

Finally it was found that grain boundaries of pre-exposed specimens contained large particles over and above those due to normal ageing. These remained dark under bright field conditons, irrespective of tilt and it was postulated that they were a zinc-rich phase, the formation of which is enhanced in moist conditions (Fig. 8).

5. Discussion of Experimental Results

The experimental results of this study strongly support the case for hydrogen involvement in the pre-exposure phenomenon. The high voltage electron metallography studies have produced direct evidence of the existence of hydrogen in pre-exposed specimens and the autoclave results indicate a behaviour best explained by a hydrogen embrittlement mechanism.

The formation of hydrogen bubbles was found to be dependent on the nature of the grain boundary. As noted in the previous section this is not unexpected as the energy required to produce the bubble must depend on the surface energy of the grain boundary/matrix interface. Essentially the process consists of the replacement of a metal-metal interface by two metal-hydrogen gas boundaries and will therefore be highly dependent upon the type of grain boundary involved and the presence or otherwise of particles at these boundaries. It seems that the grain boundary precipitates have weak interfaces with the matrix and facilitate bubble formation.

The observation that total embrittlement occurs before the appearance of bubbles suggests that it is the hydrogen dissolved in the material in the grain boundaries that causes embrittlement. This argument would suggest that, at least initially nucleation and growth of bubbles actually takes hydrogen out of solution and decreases the hydrogen activity or fugacity in the boundary. This would explain the more tolerant behaviour of overaged specimens towards exposure to water vapour. It is likely that the incoherent grain boundary particles cause bubble nucleation at lower hydrogen concentrations than is possible in material aged for shorter times.

The observation of cracks in the absence of an externally applied stress at very long pre-exposure times suggests that the combined effects of the high level of hydrogen concentration in the boundary and the bubbles are sufficient to cause cracks to propagate along the boundary (probably nucleating at the bubbles). Any internal stress would naturally enhance the cracking. The observations of cracks in the grip regions

of long term pre-exposure samples and the very rapid cracking of pre-strained specimens are both consistent with this. Pre-straining may also enhance embrittlement by breaking down, or merely thinning, the oxide film on the metal surface, and (as suggested in the previous section) by producing dislocation networks via which the rate of mass transport of hydrogen into the metal is increased.

The partial recovery in ductility in region III, of the specimens pre-exposed in the autoclave is not fully understood. However, certain important points may be made. It is known that straightforward overageing (graph I) increases the resistance to pre-exposure embrittlement and stress corrosion. In the autoclave tests overageing occurs concurrently with the uptake of hydrogen. Ductility recovery takes place after the hydrogen level has reached a high enough value to produce complete embrittlement at shorter ageing times (region II). Since a decrease in total hydrogen level cannot have occurred on entering stage III it is implied that, in the absence of hydrogen bubble formation, the overaged microstructure produced in stage III is intrinsically more tolerant to hydrogen than the microstructure characteristic of shorter ageing times.

It may be argued that in fact hydrogen bubbles do form in stage III, reducing the level of hydrogen in the grain boundary, but these are too small to see in the microscope. In fact the bubbles would have to be extremely small and present in small numbers to escape detection, and it is doubtful if, under such conditions they could produce a significant decrease in hydrogen concentration in solution. However this point requires further microscopical examination.

The characteristic three zone fracture, consisting of an inter-crystalline brittle fracture at the edges, with an intermediate trans-granular zone between it and a ductile central core, is only partially understood. It may be argued that since there is necessarily a gradient in hydrogen concentration from the sample surfaces to the centre, that the hydrogen concentration at the centre is below the critical level for embrittlement while that at the edges is above this level. This does not however explain the presence of an intervening transgranular zone. It is interesting to note that such zones have been observed previously by other workers during cathodic charging and stress corrosion tests [5,9] which further reinforces the link between hydrogen embrittlement and stress corrosion.

Consideration must be given to the lower but steadily increasing hydrogen level to be found in the grain interiors during pre-exposure. This may be expected to reduce the resistance of the grains to brittle fracture, and the onset of this may occur at lower hydrogen levels than those which produce grain boundary decohesion of this particular microstructural state. At present however, this is simply speculative and more work is required to understand the transgranular fracture zone.

Finally, after more than 36 hours, the appearance of grain boundary bubbles and the reversion to a totally intercrystalline type of failure, indicate total supersaturation of the grain boundaries with hydrogen right through the thickness of the specimen.

Zinc hydroxide penetration along grain boundaries has been reported [10] as a result of exposure to water vapour in a similar alloy, and it is likely that the large particles found in the HVEM in the grain boundaries are of similar nature. More detailed analysis is needed to clarify this point but it is significant that these were apparent only after extended pre-exposure treatments.

6. Experimental Techniques under Development and Proposed Future Work

6.1. Hydrogen Analysis

The hydrogen content of the pre-exposed specimens was considered an important parameter to be established. High temperature extraction techniques were considered unsuitable because at high temperatures reaction of any water present in the oxide film with the metal occurs leading to the production of hydrogen.

In order to avoid this error a system has been designed to carry out extraction at room temperature. It operates on the principle that aluminium, wetted by mercury, reacts readily with oxygen to form alumina.

The proposed experimental procedure is as follows:-

(a) The specimen is inserted into the reaction chamber and held above a pool of mercury. (This is achieved by attaching a piece of soft iron to the specimen and holding it in the field of a magnet external to the chamber.)

(b) The chamber is evacuated and then filled with dry high purity oxygen. The quantity of oxygen should be slightly insufficient to completely react with the aluminium.

(c) The sample is lowered magnetically into the mercury pool and is wetted. The completion of the reaction can be monitored by the stabilisation of the pressure in the chamber to a new low value.
(d) Once the pressure has stabilised its value is noted and a palladium silver tube, attached to the reaction chamber is heated by a small furnace. This makes the metal permeable to hydrogen which is then removed from the chamber. The loss of hydrogen is monitored by the further drop in pressure within the chamber.

6.2. Monocrystals

Growth of single crystals was carried out in order to determine the effect of hydrogen in the absence of grain boundaries. This aspect of the investigation has become of relevance following the observation of hydrogen induced transgranular failure of polycrystalline samples. A further important aspect which could be best examined using monocrystals is the action of dislocations on hydrogen uptake and transport.

Extension of this work to production of bicrystals with known boundaries to examine the embrittlement and bubble formation at these interfaces would be a logical progression for the future.

Paradoxically, it was found during the course of this work that growth of single crystals was more difficult in the case of the high purity base alloy than that of the commercial material. This has since been found to have been encountered by other workers [11].

The final form of the technique, which is based on a strain-anneal method is as follows:
Specimens are given a 1.8% plastic strain following an annealing treatment of 1 hour at 500°C and then lowered through a cold water heat exchanger, into a 560°C salt bath. A descent rate of 5 mm/hour was used.

6.3. In-situ Experiments

The comprehensive in situ facilities available in the H.V.E.M. are currently being employed to examine the pre-exposure phenomenon further. In particular a new modification of the existing bending stage has allowed in-situ experiments, which, have produced encouraging results. Comprehensive results will be reported in a future report. Other in-situ experiments currently in progress utilise the heating stages. The aim of this work is to examine the interaction of hydrogen bubbles and grain boundary particles during heating cycles. Previous work has shown that

the hydrogen in the thicker parts of specimen is not lost during heating up to 300°C implying that the oxide formed during electropolishing is sufficiently coherent to minimise hydrogen loss. This behaviour will therefore enable examination of the distribution of hydrogen bubbles, as the microstructure is altered by heating, from one of underaged nature to an overaged one.

It is also proposed to use the environmental cell of the EM7 microscope to examine, in situ, oxide and/or hydroxide formation, particularly along grain boundaries.

Previous work [2] has indicated the preferential formation of magnesium oxide along grain boundaries during high temperature treatment and the use of the gas reaction cell will enable in-situ examination under a wide range of environments. Of particular interest are, of course, the water vapour containing atmospheres. Also pre-cracked miniature U bend samples will be examined in a water vapour environment in order to determine the microstructural characteristics at the crack tip. These experiments will necessarily involve the use of samples with an electropolished surface, which is more resistant to cracking, hence the necessity to pre-crack first outside the microscope. Also care will be required to minimise ionisation damage during observation as it has been recently shown that pure aluminium and magnesium [12] undergo rapid reaction with water vapour at, and below, room temperature in the presence of a high flux density electron beam.

6.4. Cathodic Charging

It is proposed to carry out cathodic charging of selected tensile specimens and compare the behaviour of these with that of pre-exposed specimens. The principal aim in the use of this technique is to separate the effects of microstructure and hydrogen uptake with reference to the high temperature pre-exposure experiments (section 4.1.). The experimental conditions are similar to those used by other workers [6].

6.5. Tracer Analysis

Hydrogen evolution from pre-exposed specimens during fracture has been reported previously [2]. However, as shown then, testing under vacuum partially restores ductility and since the mass spectrometer used in these tests must operate at pressures below 10^{-6} torr it follows that the results refer to ductile failure.

In order to monitor hydrogen evolution during brittle failure it is proposed to monitor tritium evolution by means of a γ-compensated, low level ionisation chamber, if one of sufficient sensitivity can be obtained. This would enable the test to be carried out at atmospheric pressure by employing a carrier gas which flows over the strained specimen and which is then directed through the ionisation chamber.

7. Conclusions

The experimental evidence presented in this work supports a mechanism of hydrogen embrittlement in the pre-exposure embrittlement phenomenon.

It has been shown that the mode of failure is critically dependent on the concentration of hydrogen and its interaction with the microstructure. The microstructural features bearing most influence are the grain boundary nature and precipitates. These affect the partition of hydrogen between solution in the boundary and in bubbles nucleated predominantly at the grain interfaces. The concentration of hydrogen required to produce complete embrittlement varies with the ageing treatment.

Part 2. Austenitic Stainless Steel

(a) Abstract

Work commenced in October 1977 on determining the role of hydrogen in the stress corrosion cracking of sensitized austenitic stainless steel. To date work has been concentrated on the development of experimental techniques and a preliminary study of the material.

(b) Research to date

1. Material

Research is being carried out on a type 302 commercial grade stainless steel supplied by U.S. Steel Corporation.

2. Heat Treatment

The material has been solution treated at 1100°C for 2 hours in vacuo and water quenched. Sensitization treatments of from 2 hours to 24 hours at 600°C have been carried out in vacuo, and the specimens are currently undergoing examination in the TEM to determine the optimum sensitization treatment.

3. Electron Microscopy

Equipment has been built to enable electron microscope specimens to be prepared from 3 mm diameter discs.

4. Mechanical Testing

Miniature sheet tensile specimens have been prepared and heat treated.

(c) Proposed Research

1. Pre-exposure Tests

Sensitized material will be pre-exposed in an autoclave and mechanically tested.

2. Environmental tests

Apparatus is being designed to enable tensile testing to be carried out in a corrosive environment at ambient or elevated temperatures.

3. Electron Microscopy

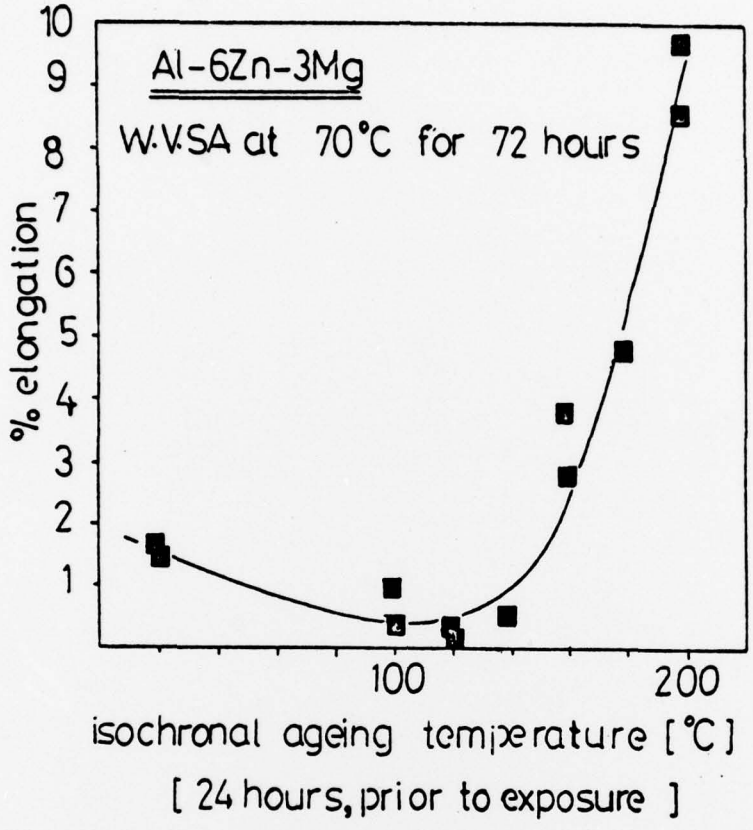
Sensitized and tested specimens (see 1 and 2 above) will be examined by scanning electron microscopy, and by high voltage electron microscopy. In particular the grain boundaries will be examined for evidence of hydrogen blistering. It is hoped to be able to obtain quantitative data on the chromium depletion at grain boundaries using the analytical facilities of a scanning transmission electron microscope (TEMSCAN).

References

1. L. Montgrain and P.R. Swann, Hydrogen in Metals, eds. I.M. Bernstein and A.W. Thompson, Metals Park, Ohio, 1974.
2. G.M. Scamans, R. Alani and P.R. Swann, Corrosion Science, 16, 443, 1976.
3. W. Gruhl, Z. Metallkde, 54, 86, 1963.
4. R. Alani, Ph.D. Thesis, London University, 1976.
5. R.J. Gest and A.R. Troiano, Corrosion, 30, 274, 1974.
6. J. Albrecht, B.J. McTiernan, I.M. Bernstein and A.W. Thompson, Scripta Met., 11, 893, 1977.
7. M.O. Speidel and M.V. Hyatt, Stress Corrosion Cracking of High Strength Aluminium Alloys, Advances in Corrosion Science and Technology, Vol. 2, 1972.
8. L.G. Lorimer, R.B. Nicholson, Acta Met., 17, 1379, 1969.
9. J.C. Scully, Research Evaluation Conference on the Theory of Stress Corrosion Cracking in Alloys (J.C. Scully, ed.) 127, Ericeila 1971.
10. G.M. Scamans and C.D. Tuck, Proc. 2nd Int. Congress on Hydrogen in Metals, Paris, 1977.
11. G.M. Scamans, Private Communication, Alcan U.K. Research Lab., Banbury, Oxon.
12. H.M. Flower, Radiation Effects, 33, 173, 1977.

TABLE 1

Alloy	Cu	Fe	Mg	Mn	Si	Ti	Zn	Cr	B	
High Purity Base	0.002	0.01	2.9	0.002	0.01	0.01	6.1	0.01	-	Balance Al
Commercial 7075	1.4	0.3	2.6	0.2	0.15	-	6.2	0.11		Balance Al



Graph I

*Each data point represents an average of six tests.

Graph II

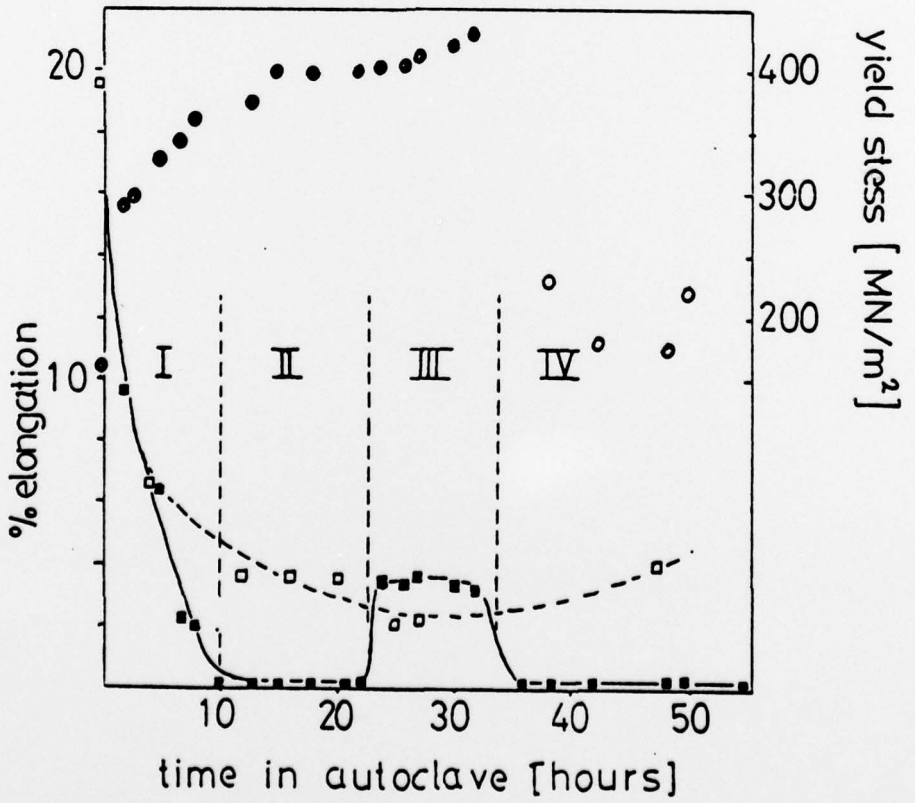
Al-6Zn-3Mg

■ Exposed to steam at 120°C*

□ Dry

○ Fracture at grips

● Yield Stress



*Each data point represents an average of six tests.

Figure 1. Brittle intercrystalline failure in a sample exposed to water vapour in autoclave for 12 hours. (Region II)
Specimen heat treatment: S.T. 450°C 1 hour,
Cold water quenched
Placed in autoclave at 120°C and
2.06 bars pressure for 12 hours.

Figure 2. Same specimen showing initiation of transgranular cracking.

Figure 3. Evidence of plastic deformation in the same specimen. Large, intermetallic particles are apparent, and are associated with large voids.

figure 1 1.5 μ

figure 2 9 μm

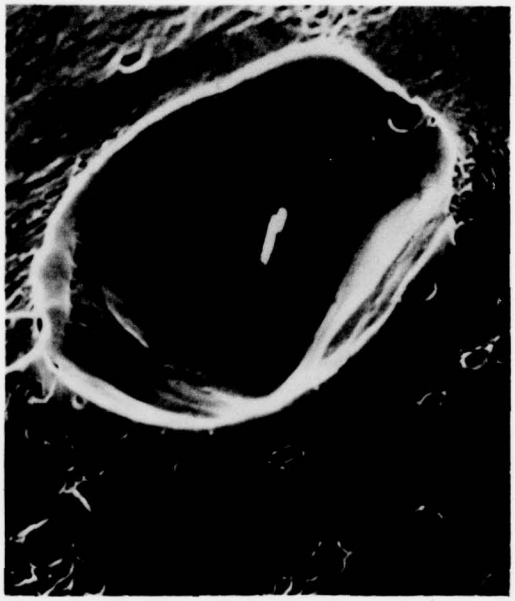


figure 3 2.5 μm

Figure 4. Fracture Surface of standard tensile specimen after 32 hours in autoclave (Region III). Note three distinct regions of fracture.
Heat treatment: S.T. 450°C 1 hour
In autoclave at 120°C and 2.06 bars pressure for 32 hours.

Figure 5. Intercrystalline failure in tensile specimen exposed to water vapour in autoclave for 50 hours (Region IV) Note the appearance of dimples and their distribution.
Heat Treatment: S.T. 450°C 1 hour
In autoclave at 120°C and 2.06 bars pressure for 50 hours.

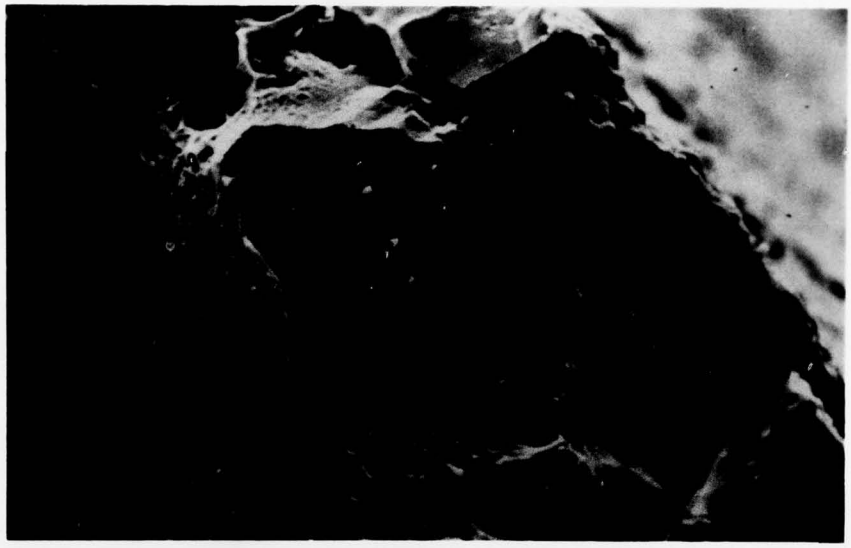


figure 4

20 µm

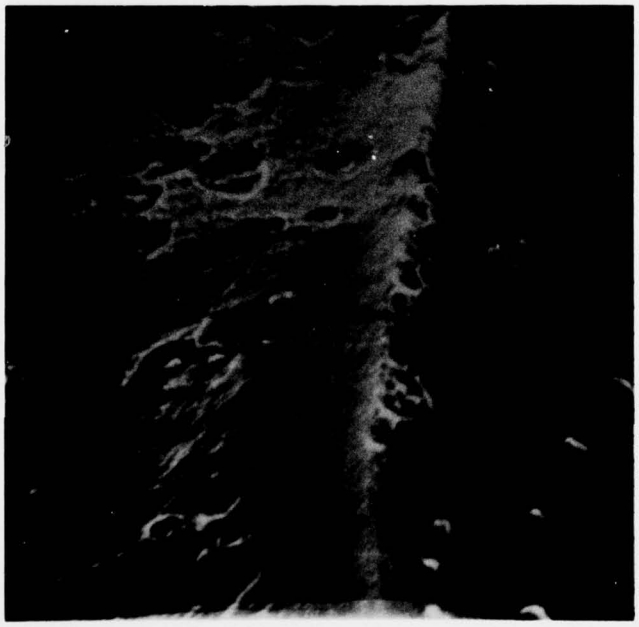


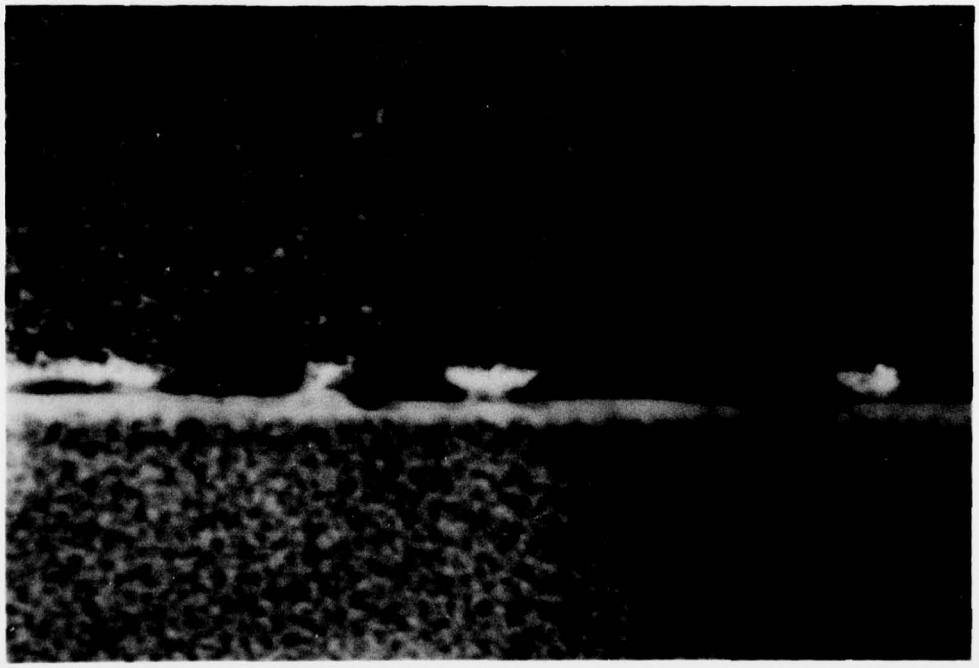
figure 5

2 µm

Figure 6(a,b). Hydrogen bubbles at grain boundary precipitate/matrix interface. (Region IV)
Heat treatment: S.T. 450°C 1 hour
Placed in autoclave at 120°C and
2.06 bars pressure for 60 hours.

0.1 μm

figure 6a



0.1 μm

figure 6b

Figure 7. T.E.M. Micrograph showing bubble formation on a dislocation attached to a grain boundary.
Note hydrogen bubbles at the grain boundary
Specimen treatment: S.T. 450°C for 1 hour
Cold water quenched
Exposed to water vapour in autoclave at 120°C and 2.06 bars pressure for 26 hours as a thin sample (0.2 mm thickness).

Figure 8. T.E.M. Micrograph showing grain boundary bubbles and precipitates, and the anomalously large particles only found in pre-exposed samples.
Heat treatment: S.T. 450°C for 1 hour
Cold water quenched
Aged at 150°C for 15 hours
Exposed for 6 days to w.v.s.a. at 70°C
as a thin, electron transparent, foil.

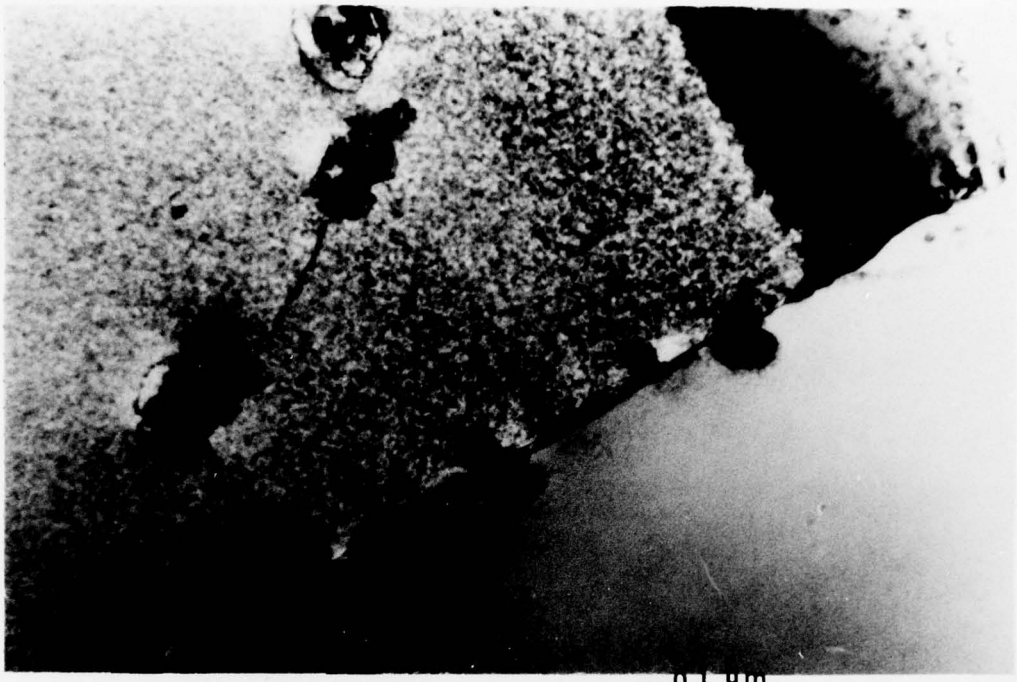


figure 7

figure 8